

CLAIMS

What is claimed is:

1. A method for electrodeposition of copper on a noble metal layer of a work piece, the method comprising the steps of:

exposing the noble metal layer to an electrodeposition composition, said electrodeposition composition comprising a copper salt, a suppressor, an accelerator and an electrolyte;

initiating electrodeposition of copper on a surface of the noble metal layer by application of a predetermined current density to the work piece; and

terminating said initiating electrodeposition upon the occurrence of a predetermined event.

2. The method of claim 1, the step of initiating electrodeposition of copper comprising subjecting said noble metal layer to a current density no greater than 40 mAmps/cm<sup>2</sup>.

3. The method of claim 2, the step of initiating electrodeposition of copper comprising subjecting said noble metal layer to a current density no greater than 20 mAmps/cm<sup>2</sup>.

4. The method of claim 1, the step of initiating electrodeposition of copper comprising subjecting said noble metal layer to at least one of a constant current, a constant voltage, a modulated current and a modulated voltage.

5. The method of claim 1, the step of exposing the noble metal layer to said electrodeposition composition comprising exposing to said electrodeposition composition a layer of at least one of ruthenium, rhodium, palladium, osmium, iridium and platinum.

6. The method of claim 1, said suppressor having a cloud point, the method further comprising selecting an electrodeposition temperature, and, if said cloud point is greater than said electrodeposition temperature, the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having an anion present in an

amount sufficient to lower said cloud point to approximately no greater than said electrodeposition temperature.

7. The method of claim 6, the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having at least one anion selected from the group comprising chloride ions, bromide ions, iodide ions and sulfate ions.

8. The method of claim 1, said suppressor having a cloud point, the method further comprising the step of selecting an electrodeposition temperature and the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having said suppressor formulated so that said cloud point matches said electrodeposition temperature.

9. The method of claim 1, the work piece having a feature and a field region and the step of exposing comprising exposing the noble metal layer to said electrodeposition composition that is formulated so that, upon the step of initiating electrodeposition of copper, the rate of deposition of the copper within said feature is greater than the rate of deposition of the copper on said field region.

10. The method of claim 1, wherein the work piece has a first field region adjacent a feature having a dimension of at least 2  $\mu\text{m}$  and has a second field region adjacent a feature having a dimension of less than 2  $\mu\text{m}$ , and wherein the step of exposing comprises exposing the noble metal layer to said electrodeposition composition formulated so that said suppressor exhibits preferential adsorption on said first and said second field regions.

11. The method of claim 1, the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having said suppressor that comprises a wetting agent.

12. The method of claim 1, the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having said suppressor comprising a block copolymer of ethylene oxide and propylene oxide.

13. The method of claim 1, the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having said suppressor comprising at least

one selected from the group comprising Pluronic®, Pluronic® R, Tetronic®, and Tetronic® R surfactants.

14. The method of claim 1, the work piece having a first feature with a dimension of at least 2  $\mu\text{m}$  wide and having a second feature with a dimension of less than 2  $\mu\text{m}$ , wherein the step of exposing comprises exposing the noble metal layer to said electrodeposition composition formulated so that said accelerator exhibits preferential adsorption within said first and said second features.

15. The method of claim 1, the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having said accelerator comprising at least one sulfur atom.

16. The method of claim 1, the step of exposing comprising exposing the noble metal layer to said electrodeposition composition having said accelerator formed of one of a metal salt of 2-mercaptoethane sulfonic acid and a metal salt of 3-mercaptopropane sulfonic acid.

17. The method of claim 1, the method of electrodeposition comprising a method for electroplating.

18. The method of claim 1, the method of electrodeposition comprising a method for electrochemical mechanical deposition.

19. The method of claim 1, wherein the step of initiating electrodeposition of copper results in the deposition of a copper metallization layer on the work piece and the step of terminating comprises terminating the step of initiating electrodeposition of copper when said copper metallization layer has a thickness in the range of about 500 to about 3000 angstroms.

20. A method for electrodeposition of copper on a noble metal layer of a work piece, the method comprising the steps of:

forming a first layer of copper overlying the noble metal layer;

exposing the work piece to a first solution of copper ions;

initiating electrodeposition of copper overlying said first layer of copper by application of a predetermined current density to the work piece; and

terminating said step of initiating electrodeposition of copper upon the occurrence of a predetermined event.

21. The method of claim 20, the step of forming a first layer of copper comprising the step of forming a copper seed layer overlying the noble metal layer.

22. The method of claim 21, wherein the step of forming a copper seed layer comprises the steps of:

exposing the noble metal layer to a second solution comprising copper ions; and

exposing the noble metal layer to a copper reducing agent.

23. The method of claim 21, wherein the step of forming said copper seed layer comprises forming said copper seed layer to a thickness no greater than approximately 500 angstroms.

24. The method of claim 22, the step of exposing the noble metal layer to a copper reducing agent comprising exposing the noble metal layer to at least one compound selected from the group comprising glycolic acid, glyoxal, a sugar, an alcohol, a polyhydroxy acid, and a polyhydroxy aldehyde.

25. The method of claim 22, the step of exposing the noble metal layer to a second solution comprising exposing the noble metal layer to said second solution having a complexing agent.

26. The method of claim 25, the step of exposing the noble metal layer to said second solution having a complexing agent comprising exposing the noble metal layer to at least one of ethylenediaminetetraacetic acid, triethylenetetraamine, diethylenetriamine and 1,2 diaminocyclohexanetetraacetic acid.

27. The method of claim 22, wherein said second solution comprises a complexing agent, and wherein the step of exposing the noble metal layer to a copper reducing agent comprises adding said reducing agent to said second solution drop wise.

28. The method of claim 22, wherein said second solution comprises a complexing agent, and wherein the step of exposing the noble metal layer to a copper reducing agent comprises exposing the noble metal layer to said second solution having a supersaturation of reducing agent.

29. The method of claim 28, the step of exposing the noble metal layer to said second solution having a supersaturation of reducing agent further comprising the step of achieving said supersaturation by adding approximately drop wise to said second solution an amount of reducing agent suitable for forming a supersaturation.

30. The method of claim 28, the step of exposing the noble metal layer to said second solution having a supersaturation of reducing agent further comprising the step of achieving said supersaturation by adding approximately all at once to said second solution an amount of reducing agent suitable for forming a supersaturation.

31. The method of claim 22, the step of forming a copper seed layer comprising maintaining a pH of said second solution in the range of about 1 to 14.

32. The method of claim 31, the step of forming a copper seed layer comprising maintaining a pH of said second solution in the range of about 10 to 14.

33. The method of claim 32, the step of forming a copper seed layer comprising maintaining a pH of said second solution in the range of about 11 to 13.

34. The method of claim 21, the step of forming a copper seed layer comprising the step of subjecting the noble metal layer to a current density.

35. The method of claim 34, the step of forming a copper seed layer comprising the step of subjecting the noble metal layer to a current density no greater than 20 mAmps/cm<sup>2</sup>.

36. The method of claim 20, the step of initiating electrodeposition of copper comprising the step of subjecting the work piece to a current density no greater than 40 mAmps/cm<sup>2</sup>.

37. The method of claim 36, the step of initiating electrodeposition of copper comprising the step of subjecting the work piece to a current density no greater than 20 mAmps/cm<sup>2</sup>.

38. The method of claim 20, said step of initiating electrodeposition of copper comprising subjecting the noble metal layer to at least one of a constant current, a constant voltage, a modulated current and a modulated voltage.

39. The method of claim 20, wherein said step of initiating electrodeposition of copper causes a copper metallization layer to form overlying said copper seed layer and the step of terminating comprises terminating said initiating electrodeposition of copper upon said copper metallization layer having a thickness in the range of about 500 to 3000 angstroms.

40. The method of claim 20, the step of forming a first layer of copper comprising the step of exposing the noble metal layer to an electrodeposition composition comprising a copper salt, a suppressor, an accelerator, and an electrolyte.

41. The method of claim 20, the step of forming a first layer of copper comprising forming a first layer of copper overlying the noble metal layer formed from at least one of ruthenium, rhodium, palladium, osmium, iridium and platinum.

42. The method of claim 20, the step of exposing the work piece to a first solution of copper ions comprising the step of exposing the work piece to an electrodeposition composition comprising a copper salt, a suppressor, an accelerator, and an electrolyte.

43. The method of claim 42, wherein said suppressor has a cloud point, the method further comprises the step of selecting an electrodeposition temperature and, if said cloud point is greater than said electrodeposition temperature, the step of exposing the work piece to a first solution of copper ions comprises exposing the work piece to said electrodeposition composition having an anion present in an amount sufficient to lower said cloud point to approximately no greater than said electrodeposition temperature.

44. The method of claim 43, wherein said suppressor has a cloud point, the method further comprises the step of selecting an electrodeposition temperature and the step of exposing the work piece to a first solution of copper ions comprises exposing the work

piece to said electrodeposition composition having said suppressor formulated so that said cloud point matches said electrodeposition temperature.

45. The method of claim 44, the step of exposing the work piece to a first solution of copper ions comprising exposing the work piece to said electrodeposition composition having at least one anion selected from the group comprising chloride ions, bromide ions, iodide ions and sulfate ions.

46. The method of claim 42, wherein the step of exposing the work piece to a first solution of copper ions comprises exposing the work piece to said electrodeposition composition having said suppressor comprising a wetting agent.

47. The method of claim 42, the step of exposing the work piece to a first solution of copper ions comprising exposing the work piece to said electrodeposition composition having said suppressor comprising a block copolymer of ethylene oxide and propylene oxide.

48. The method of claim 42, the step of exposing the work piece to a first solution of copper ions comprising exposing the work piece to said electrodeposition composition having said suppressor comprising at least one selected from the group comprising Pluronic®, Pluronic® R, Tetronic®, and Tetronic® R surfactants.

49. The method of claim 42, the step of exposing the work piece to a first solution of copper ions comprising exposing the work piece to said electrodeposition composition having said accelerator comprising at least one sulfur atom.

50. The method of claim 49, the step of exposing the work piece to a first solution of copper ions comprising exposing the work piece to said electrodeposition composition having said accelerator comprising one of a metal salt of 2-mercaptopethane sulfonic acid and a metal salt of 3-mercaptopropane sulfonic acid.

51. The method of claim 20, the method of electrodeposition comprising a method for electroplating.

52. The method of claim 20, the method of electrodeposition comprising a method for electrochemical mechanical deposition.

53. A method for electrodeposition of copper on a work piece, the method comprising the steps of:

depositing a barrier layer of noble metal overlying the work piece;

exposing the barrier layer to a first solution of copper ions;

subjecting the work piece to a current density no greater than 20 mAmps/cm<sup>2</sup> to form a copper metallization layer overlying said barrier layer; and

terminating said subjecting when said copper metallization layer achieves a thickness in the range of from about 500 angstroms to about 3000 angstroms.

54. The method of claim 53, the method further comprising the step of forming a copper seed layer overlying said barrier layer before the step of exposing and after the step of depositing.

55. The method of claim 54, wherein the step of forming a copper seed layer comprises the steps of:

exposing said barrier layer to a second solution comprising copper ions; and

exposing said barrier layer to a copper reducing agent.

56. The method of claim 54, wherein the step of forming said copper seed layer comprises forming said copper seed layer to a thickness no greater than approximately 500 angstroms.

57. The method of claim 55, the step of exposing said barrier layer to a copper reducing agent comprising the step of exposing said barrier layer to at least one selected from the group comprising glycolic acid, glyoxal, a sugar, an alcohol, a polyhydroxy acid, and a polyhydroxy aldehyde.

58. The method of claim 55, the step of forming a copper seed layer further comprising the step of exposing said barrier layer to a complexing agent.

59. The method of claim 58, the step of exposing said barrier layer to a complexing agent comprising exposing said barrier layer to at least one of

ethylenediaminetetraacetic acid, triethylenetetraamine, diethylenetriamine, and 1,2 diamino-cyclohexanetetraacetic acid.

60. The method of claim 54, the step of forming a copper seed layer comprising the step of subjecting said barrier layer to a current density.

61. The method of claim 53, the step of depositing a barrier layer of noble metal comprising depositing a layer of at least one selected from the group comprising ruthenium, rhodium, palladium, osmium, iridium and platinum.

62. The method of claim 53, the step of depositing a barrier layer of noble metal comprising depositing said barrier layer of noble metal to a thickness no greater than 400 angstroms.

63. The method of claim 53, wherein the step of exposing said barrier layer to a first solution of copper ions comprises the steps of formulating an electrodeposition composition comprising a copper salt, a suppressor, an accelerator, and an electrolyte and exposing said barrier layer to said electrodeposition composition.

64. The method of claim 63, wherein said suppressor has a cloud point, the method further comprises the step of selecting an electrodeposition temperature and, if said cloud point is greater than said electrodeposition temperature, the step of formulating comprises combining at least one of said copper salt, said suppressor, said accelerator, and said electrolyte with an anion present in an amount sufficient to lower said cloud point to approximately no greater than said electrodeposition temperature.

65. The method of claim 63, the step of formulating further comprising formulating said electrodeposition composition to comprise at least one anion selected from the group comprising chloride ions, bromide ions, iodide ions and sulfate ions.

66. The method of claim 63, the step of formulating comprising the step of selecting a suppressor that comprises a wetting agent.

67. The method of claim 63, the step of formulating comprising the step of selecting a suppressor comprising a block copolymer of ethylene oxide and propylene oxide.

68. The method of claim 63, the step of formulating comprising the step of selecting a suppressor comprising at least one selected from the group comprising Pluronic®, Pluronic® R, Tetronic®, and Tetronic® R surfactants.

69. The method of claim 63, the step of formulating comprising the step of selecting an accelerator having at least one sulfur atom.

70. The method of claim 63, the step of formulating comprising the step of selecting an accelerator comprising one of a metal salt of 2-mercaptoethane sulfonic acid and a metal salt of 3-mercaptopropane sulfonic acid.